Comparative studies on Tb (III)-selective PVC membrane sensors

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ABSTRACT

A new terbium selective sensor based on N-(2-hydroxyphenyl)-3-(2-hydroxyphenylhydroxyphenylimino)-N-phenylbutanamidine (L_1) and N,N′-bis((1H-indole-3-yl)methylene)butane-1,4 diamine (L_2) as a ionophore is reported. Effect of various plasticizers; 2-nitrophenyloctylether (*o*-NPOE), dibutyl butylphosphonate (DBBP), chloronaphthelene (CN), dioctylphthalate (DOP) and tri-(2-ethylhexyl)phosphate (TEHP) with anion excluder, potassium tetrakis (p-chlorophenyl)borate (KTpClPB) have been studied. The membrane with a composition of ionophore (L_1):KTpClPB:PVC:*o*-NPOE (w/w, %) in ratio of 3.0:5.0:30.0:62.0 exhibited enhanced selectivity towards terbium ions (III) in the concentration range of 3.5×10^{-7} to 1.0×10^{-2} M with a detection limit of 1.2×10^{-7} M and a Nernstian slope (20.0 ± 0.5 mV dec^{-1} activity). The sensors showed the working pH range to be 3.5–7.5 with response time of 11 s. The sensor has been found to work satisfactorily in partially non-aqueous media up to 15% (v/v) content of methanol, ethanol or acetonitrile and could be used for a period of 3 months. The selectivity coefficients indicated high selectivity for terbium (III). The fast and stable response, good reproducibility and long-term stability of the sensors were observed. The application of the sensor has been demonstrated in determination of terbium (III) ions in spiked water samples.

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1. Introduction

Terbium is a rare and expensive element. It is used in lasers, semiconductor devices, colour television tubes, magnetic and computer memories. It is used to dope in calcium fluoride, calcium tungstate and strontium molybdate materials that are in turn used in solid-state devices [1]. Terbium and other elements of lanthanide group are used for gasoline-cracking catalysts, carbon arcs and in movie projectors [2]. Nowadays, the determination of terbium is important because of its importance in industries and in bio-inorganic and inorganic chemistry. Terbium is toxic by ingestion and its powder and compounds are very irritating if they come in contact with the skin and the eyes. Hence, the monitoring of terbium in environmental sample is crucial. Nowadays, a number of methods have been reported for the determination of terbium in real sample analysis, such as, electron spin resonance, induced coupled plasma mass spectroscopy, atomic emission spectrometry, high resolution-spectroscopy, laser based multistep resonance ionization, and spectrofluorimetric methods [3–6] have been used for terbium assay in various samples. All these methods are either time consuming, involve multiple sample manipulations, or are too expensive for most analytical laborato-

ries. Thus, the development of a convenient and direct method for the assay of terbium ion in different samples is of urgent need.

Ion-selective sensors have exhibited effective tools for analysis of different metal ions, anions and molecules. They are very easy to use, inexpensive, non-destructive and adaptable to small volume of sample, remain unaffected by sample colour or turbidity and gives reliable result in a wide concentration range. In view of such advantages, a number of Tb (III) selective sensors have been reported using PVC membrane [7–10]. These sensors have a limited use for the determination of terbium ions due to their poor detection limit and narrow concentration range. Thus, there is still a need for a good sensor for terbium. Schiff bases (SB) have been found to act as ion carriers in the polymeric membrane. The geometric and cavity control of host–guest complexation and modulation of lipophilicity in SB provide remarkable selectivity, sensitivity and stability for specific ion. Thus, new ionophores attracted increasing consideration for determining metals such as UO_2^{2+} [11], Cr^{3+} [12], Pb^{2+} [13], Co^{2+} [14], Ni^{2+} [15] and MoO_4^{2-} [16].

Recently we have developed a number of sensors for ions of the lanthanide group elements such as Nd^{3+} [17], Pr^{3+} [18], Ce^{3+} [19] and La^{3+} [20]. In this paper we have reported the development of terbium selective sensor and their comparative studies based on newly synthesized Schiff bases N-(2-hydroxyphenyl)-3-(2-hydroxyphenylhydroxyphenylimino)-N-phenylbutanamidine (L_1) and N,N′-bis((1H-indole-3-yl)methylene)butane-1,4 diamine (L_2).

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2. Experimental

2.1. Reagent and solution

1,4 Diamine butane, indole 3-aldehyde, o-aminophenol and 3-oxo-N-phenylbutanamide were obtained from Merck Co. and used as received. For membrane preparation, high molecular weight polyvinyl chloride (PVC), o-nitrophenyloctylether (o-NPOE), dibutylphthalate (DBP), dibutyl butylphosphonate (DBBP), dioctylphthalate (DOP), tri-(2-ethylhexyl)phosphate (TEHP) and tetrahydrofuran (THF) were used as received from Fluka. Potassium tetrakis (p-chloropheny1)borate (KTpClPB) and chloronaphthelene (CN) Sisco Research Lab. (Mumbai, India). Reagent grade terbium (III) chloride was purchased from Loba chemie, India. HPLC-grade n-hexane and methanol were obtained from Ranbaxy India. The standard Tb (III), was purchased from CDL, Calcutta, India. All potentiometric measurements were performed at room temperature using Thermo Orion 4 star pH meter.

2.2. Synthesis of ionophores

2.2.1. Synthesis of N-(2-hydroxyphenyl)-3-(2-hydroxyphenylhydroxyphenylimino)-N-phenylbutanamidine (L_1)

The ligand (Fig. 1, L_1) was prepared by condensation of 0.05 mol of 2-aminophenol and 0.025 mol of 3-oxo-N-phenylbutanamide in methanol under reflux for 6 h. A yellow colour solution was formed and precipitation of ligand was obtained after evaporation of methanol. The precipitation was washed with diethyl ether and recrystallized in methanol. The compound was stable at room temperature. Anal. Calc. for [$C_{27}H_{19}N_3O_2$]: C, 73.52; H, 5.89; N, 11.69; O, 8.90%. Found: C, 73.60; H, 5.90; N, 11.70; O, 8.90. The ^{1}H NMR (CDCl$_3$) exhibited signals at: δ (ppm): 7.5–8.5 (m, 13H), 5.0 (S, 1H), 1.2 (S, 3H), 1.5 (S, 2H), $\nu_{C=N}$: 1650 cm^{-1}.

2.2.2. Synthesis of N,N′-bis((1H-indole-3-yl)methylene)butane-1,4 diamine (L_2)

The ligand (Fig. 2, L_2) was synthesized by refluxing 0.025 mol of 1,4 diamino butane and 0.05 mol of indole-3-aldehyde in ethanol for 3 h on a water bath and cooling the reaction mixture. A yellow colour solution of reaction mixture was formed. The ligand was precipitated after evaporation of ethanol. The ligand was washed with diethyl ether and dried under vacuum. The compound was stable at room temperature. Anal. Calc. for [$C_{22}H_{22}N_4$]: C, 77.16; H, 6.48; N, 16.36%. Found: C, 77.15; H, 6.45; N, 16.38. The ^{1}H NMR (CDCl$_3$) exhibited signals at: δ_H (ppm): 7.0–7.8 (m, 10 H), 10.5 (s, 2H), 7.0 (s, 2H), 1.5–2.0 (m, 8H), $\nu_{C=N}$:1633 cm^{-1}.
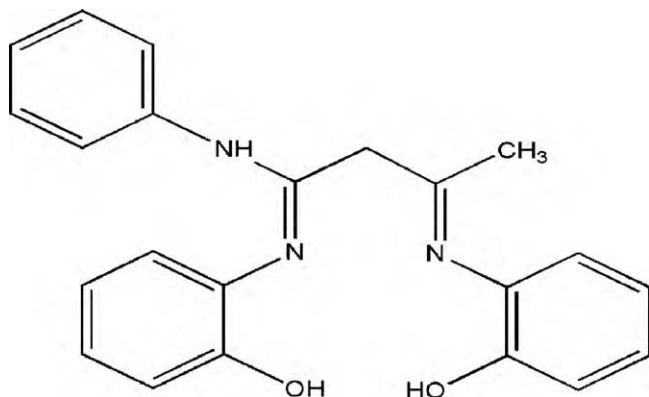

Fig. 1. Structure of ionophore N-(2-hydroxyphenyl)-3-(2-hydroxyphenylhydroxyphenylimino)-N-phenylbutanamidine (L_1).
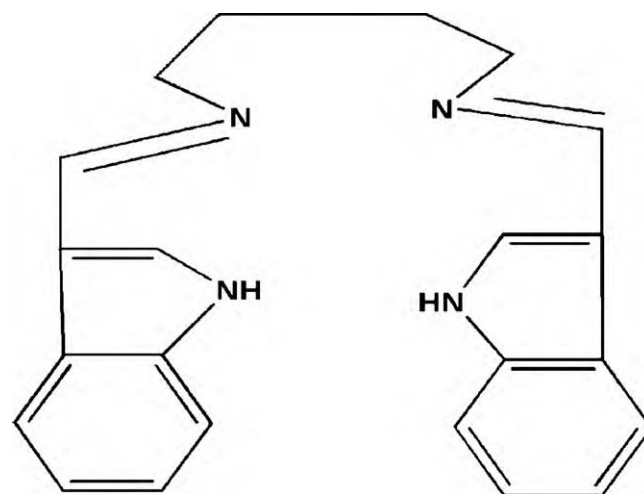

Fig. 2. Structure of ionophore N,N′-bis((1H-indole-3-yl)methylene)butane-1,4 diamine (L_2).

3. Results and discussion

3.1. Investigation of membrane composition

All the membranes were equilibrated in 0.01 M Tb (III) before starting any potential measurements. Studies revealed that a minimum of 3 days equilibration was necessary for generating reproducible and stable potentials.

The polymeric membrane sensors for Tb (III) ion based on ionophores were examined at various concentrations of internal reference TbCl$_3$ solution in the range of (1.0×10^{-1} to 1.0×10^{-3} M) and the potential response of the sensors were observed. It was found that the best results in terms of slope and working concentration range were obtained with internal solution of activity 1.0×10^{-2} M. Thus, 1.0×10^{-2} M concentration of the reference solution was appropriate for the proper working of the sensors. The potentials were measured by varying the concentration of Tb (III) in the test solution in the range of 1.0×10^{-9} to 1.0×10^{-2} M at pH 4.5 with a digital potentiometer (model 5652 A, ECIL, India) by setting up the following cell assembly, employing saturated calomel electrodes (SCE) as a reference electrode.
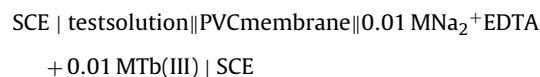
SCE | testsolution‖PVCmembrane‖0.01 MNa$_2$$^+$EDTA

+ 0.01 MTb(III) | SCE

The activity of Tb (III) ions was calculated using modified form of the Debye–Huckel equation [21].

The ratio of both ionophores and membrane ingredients were optimized so as to obtain membranes which gave best performance characteristics. The resulting data are presented in Table 1. It can be seen from Table 1 that the sensor nos. 1 and 14 having the membrane without ionophores (L_1 and L_2) exhibits nil response. The poor working range of membrane sensors (2 and 15); 4.5×10^{-3} to 1.0×10^{-2} M, 7.5×10^{-4} to 1.0×10^{-2} M can be easily understood by lack of proper lipophilicity without plasticizers with a sub-Nernstian slopes of 16.1 ± 0.5 and 17.8 ± 0.5 mV dec^{-1} activity respectively. The slope of the membranes is non-Nernstian and the working concentration ranges were found to be narrow. Therefore, it was necessary to improve performance of these membranes based on (L_1) and (L_2).

It is well known that the sensitivity and selectivity of cation-selective membrane sensors strongly depend on the membrane composition and the nature of the plasticizer used [22–24]. To get the best results, membrane compositions have been optimized using different concentration of plasticizers having a different

Table 1
Optimization of membranes composition of terbium sensors. Bold indicates the best performing membrane.

Sensor no.	Composition of membrane sensors (w/w, %)				Working range (M)	Slope ± 0.5	Response time (s)
	Ionophore	PVC	Additives	Plasticizer			
1	0.0 (L_1)	30.0	5.0 (KTpClPB)	66.0	–	–	22
2	13.0 (L_1)	73.0	14.0 (KTpClPB)	0.0	4.5×10^{-3} to 1.0×10^{-2}	16.0	26
3	3.0 (L_1)	30.0	5.0 (KTpClPB)	63.0 (DBP)	5.5×10^{-6} to 1.0×10^{-2}	17.6	18
4	3.0 (L_1)	30.0	5.0 (KTpClPB)	63.0 (DBBP)	7.4×10^{-5} to 1.0×10^{-2}	16.8	20
5	3.0 (L_1)	30.0	5.0 (KTpClPB)	63.0 (TEHP)	6.8×10^{-5} to 1.0×10^{-2}	17.0	19
6	3.0 (L_1)	30.0	5.0 (KTpClPB)	63.0 (CN)	2.4×10^{-5} to 1.0×10^{-2}	18.0	16
7	3.0 (L_1)	30.0	5.0 (KTpClPB)	63.0 (DOP)	4.4×10^{-5} to 1.0×10^{-2}	17.8	14
8	**3.0 (L_1)**	**30.0**	**5.0 (KTpClPB)**	**62.0 (o-NPOE)**	**3.5×10^{-7} to 1.0×10^{-2}**	**20.0**	**11**
9	4.0 (L_1)	30.0	5.0 (KTpClPB)	61.0 (o-NPOE)	7.5×10^{-7} to 1.0×10^{-2}	19.5	11
10	5.0 (L_1)	30.0	5.0 (KTpClPB)	60.0 (o-NPOE)	1.2×10^{-6} to 1.0×10^{-2}	19.3	13
11	6.0 (L_1)	30.0	5.0 (KTpClPB)	59.0 (o-NPOE)	6.5×10^{-6} to 1.0×10^{-2}	18.6	12
12	3.0 (L_1)	25.0	5.0 (KTpClPB)	67.0 (o-NPOE)	4.5×10^{-7} to 1.0×10^{-2}	20.0	11
13	3.0 (L_1)	35.0	5.0 (KTpClPB)	57.0 (o-NPOE)	5.5×10^{-6} to 1.0×10^{-2}	18.3	15
14	0.0 (L_2)	30.0	5.0 (KTpClPB)	66.0	–	–	24
15	13.0 (L_2)	73.0	14.0 (KTpClPB)	0.0	7.5×10^{-4} to 1.0×10^{-2}	17.8	14
16	3.0 (L_2)	30.0	5.0 (KTpClPB)	63.0 (DBP)	5.3×10^{-5} to 1.0×10^{-2}	18.9	15
17	3.0 (L_2)	30.0	5.0 (KTpClPB)	63.0 (DBBP)	9.5×10^{-5} to 1.0×10^{-2}	18.5	15
18	3.0 (L_2)	30.0	5.0 (KTpClPB)	63.0 (TEHP)	8.5×10^{-5} to 1.0×10^{-2}	18.7	14
19	3.0 (L_2)	30.0	5.0 (KTpClPB)	63.0 (CN)	6.4×10^{-5} to 1.0×10^{-2}	18.8	12
20	3.0 (L_2)	30.0	5.0 (KTpClPB)	63.0 (DOP)	7.5×10^{-5} to 1.0×10^{-2}	19.2	13
21	**3.0 (L_2)**	**30.0**	**5.0 (KTpClPB)**	**62.0 (o-NPOE)**	**3.1×10^{-6} to 1.0×10^{-2}**	**19.5**	**15**
22	4.0 (L_2)	30.0	5.0 (KTpClPB)	61.0 (o-NPOE)	5.1×10^{-6} to 1.0×10^{-2}	19.0	15
23	5.0 (L_2)	30.0	5.0 (KTpClPB)	60.0 (o-NPOE)	1.5×10^{-5} to 1.0×10^{-2}	18.6	17
24	6.0 (L_2)	30.0	5.0 (KTpClPB)	59.0 (o-NPOE)	5.3×10^{-5} to 1.0×10^{-2}	18.5	16
25	3.0 (L_2)	25.0	5.0 (KTpClPB)	67.0 (o-NPOE)	4.6×10^{-6} to 1.0×10^{-2}	19.4	15
26	3.0 (L_2)	35.0	5.0 (KTpClPB)	57.0 (o-NPOE)	6.1×10^{-5} to 1.0×10^{-2}	18.2	18

dielectric constants (ε); TEHP ($\varepsilon = 4.8$), DBBP ($\varepsilon = 4.6$), DBP ($\varepsilon = 6.4$), o-NPOE ($\varepsilon = 24$), CN ($\varepsilon = 5$), DOP ($\varepsilon = 5$) and PVC ($\varepsilon = 3.9$). The effect of plasticizers on Tb (III) selective membrane sensors based on L_1 and L_2 ligands is shown in Table 1. It is clear from Table 1 that o-NPOE is more effective plasticizer than others in preparing the Tb (III) ISEs because of its high dielectric ($\varepsilon = 24$) constant that increases the Tb (III) selectivity for proposed ionophores. The plasticizers except o-NPOE have less dielectric constant therefore they will solvate the extracted cations in ionophore-free membranes or membrane segments more strongly than o-NPOE-based membranes, which lead to smaller binding constants. We have also plotted the characteristic response graph (Figs. 3 and 4) of membrane sensors based on L_1 and L_2 ligands respectively for different proposed plasticizers. It is clear from Figs. 3 and 4 that o-NPOE ($\varepsilon = 24$) showed the highest selectivity for (L_1) and (L_2) based membrane sensors. The results

presented in Table 1 also showed that the o-NPOE ($\varepsilon = 24$) plasticizer exhibited wide working concentration range 3.5×10^{-7} to 1.0×10^{-2} M (sensor no. 8, based on L_1), 3.1×10^{-6} to 1.0×10^{-2} M (sensor no. 21, based on L_2) with Nernstian slope of 20.0 ± 0.5 and 19.5 ± 0.5 mV dec^{-1} activity, for (L_1) and (L_2) ionophores, respectively.

The properties of ion-selective sensors (ISEs) based on neutral ionophores are strongly influenced by the ionic sites in their membranes. To determine the effect of different lipophilic anionic additives added to the membrane phase influencing the working sensitivity of the sensor, a series of membranes was studied by using lipophilic additives like NaTPB, KTpClPB and OA (Table 2). Incorporating KTpClPB in the membrane composition in the proportion of 5.0% (w/w) relative to the total membrane composition showed best performance characteristics. This is due to the fact that
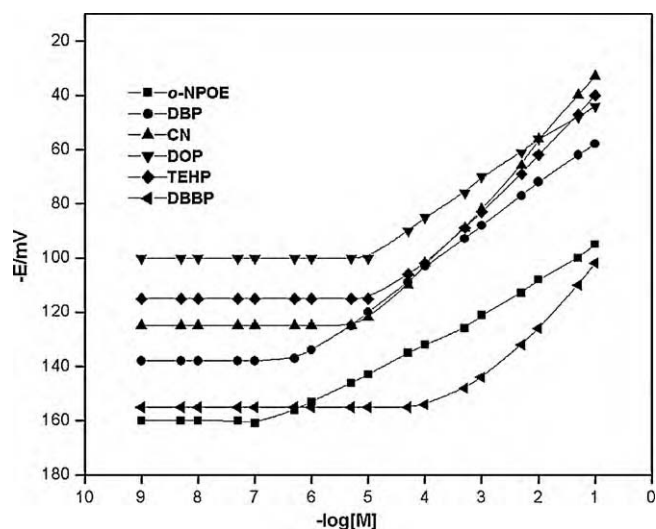

Fig. 3. Variation of membrane potential with activity of Tb (III) ions, of PVC based membranes of L_1 with plasticizers: (1) o-NPOE, (2) DBP, (3) CN, (4) DOP, (5) TEHP and (6) DBBP.

Fig. 4. Variation of membrane potential with activity of Tb (III) ions, of PVC based membranes of L_2 with plasticizers: (1) o-NPOE, (2) DBP, (3) CN, (4) DOP, (5) TEHP and (6) DBBP.
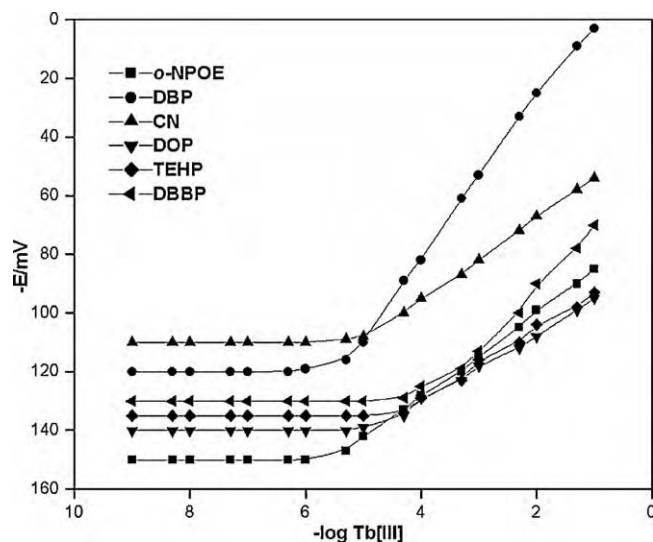
Table 2
The effect of anionic additives on the performances of Tb (III) selective sensors. Bold indicates the best performing membrane.

Membrane sensor composition	Anionic additives	Working concentration range (M)	Detection limit ± 0.5 (M)	Slope ± 0.5[*]
	–	5.5×10^{-4} to 1.0×10^{-2}	4.6×10^{-4}	16.0
	KTpClPB	**3.2×10^{-7} to 1.0×10^{-2}**	**1.2×10^{-7}**	**20.0**
L_1:PVC:o-NPOE (w/w, %) 3.0:30.0:63.0:5.0 (anionic additive)	NaTPB	3.5×10^{-6} to 1.0×10^{-2}	2.5×10^{-6}	19.5
	OA	3.4×10^{-5} to 1.0×10^{-2}	2.8×10^{-5}	18.8
	–	4.3×10^{-3} to 1.0×10^{-2}	3.5×10^{-3}	16.5
	KTpClPB	**3.1×10^{-6} to 1.0×10^{-2}**	**1.2×10^{-6}**	**19.5**
L_2:PVC:o-NPOE (w/w, %) 3.0:30.0:62.0:5.0 (anionic additive)	NaTPB	2.3×10^{-5} to 1.0×10^{-2}	1.5×10^{-5}	19.4
	OA	3.3×10^{-5} to 1.0×10^{-2}	2.6×10^{-5}	18.3

[*] mV dec^{-1} of activity.

KTpClPB acts as a charge compensating counter ion in the membrane and thus facilitate the process of ion charge transduction.

3.2. Potentiometric calibration characteristics of sensors

After optimization of membrane composition of sensors based on ligand (L_1 and L_2), the best optimized membrane sensors (8 and 21) were further calibrated against the standard solution of Tb (III) using a Tris–HCl (pH = 4.5) buffer to get the calibration graph (Fig. 5). The results thus obtained indicate that the sensor no. 8 based on (L_1) as an ionophore in PVC membrane with optimized composition (L_1):KTpClPB:PVC:o-NPOE (w/w, mg) in ratio of 3.0:5.0:30.0:62.0 exhibited Nernstian slope (20.0 ± 0.5 mV dec^{-1} activity) over a wide concentration range of 3.5×10^{-7} to 1.0×10^{-2} M with a limit of detection 1.2×10^{-7} M while sensor no. 21 based on (L_2) with same optimized composition (L_2):KTpClPB:PVC:o-NPOE (w/w, %) in ratio of 3.0:5.0:30.0:62.0 exhibited Nernstian slope (19.5 ± 0.5 mV dec^{-1} activity) and concentration range of 3.1×10^{-6} to 1.0×10^{-2} M with limit of detection 2.3×10^{-6} M. The potentiometric characteristics of proposed sensors (nos. 8 and 21) were further compared with the reported sensors (Table 6).

3.3. Influence of pH on the sensors performance

The dependence of sensor's potential response was investigated over the pH range 2.0–8.5 for 1.0×10^{-3} and 1.0×10^{-4} M Tb (III) solution (Fig. 6). The operational range was studied by varying the pH of the test solution with nitric acid or sodium hydroxide (0.1 M). As can be seen from Fig. 6, the potential is independent of pH in the range 3.5–7.5 and 3.0–7.5 for sensor nos. 8 and 21 based on L_1 and

L_2, respectively. Therefore, the same was taken as the working pH range of the sensor assemblies. The increase in potential below pH 3 is mainly due to the contribution of H$^+$ ions in transport mechanism over the Tb (III) ions. Similarly above pH 7.5, the contribution of OH$^-$ ions observed as a precipitation of Tb(OH)$_3$, resulting in the reduction of potential.

3.4. Dynamic response and life time

It is well known that the dynamic response and life time of a sensor are one of the most important factors in its evaluation. To measure the dynamic response time of the proposed sensor the concentration of the test solution has been successively changed from 1.0×10^{-6} to 1.0×10^{-1} M. The resulting data depicted in Fig. 7, shows that the time needed to reach a potential with in ±1 mV of the final equilibrium value after successive immersion of a series of Tb (III) ions, and each having a tenfold difference in concentration is 11 for sensor no. 8. This is most probably due to the fast exchange kinetics of complexation–decomplexation of Tb (III) ions with the L_1 ionophore at the test solution–membrane interface.

The degradation of the sensitivity in the polymeric membrane may be dependent upon the lipophilicity and chemical stability of the ionophores, which can result in the ionophore bleeding from the membrane. Since Tb (III) chelates of ionophores are the compounds having high lipophilicity, the membranes containing them should provide very low bleeding of the ionophore. The membrane could be used over a period of 3 months for sensor based on L_1 (no. 8) and 2.5 months for sensor based on L_2 (no. 21). However, it is important to emphasize that it should be stored in 0.01 M Tb (III) solution when not in use.
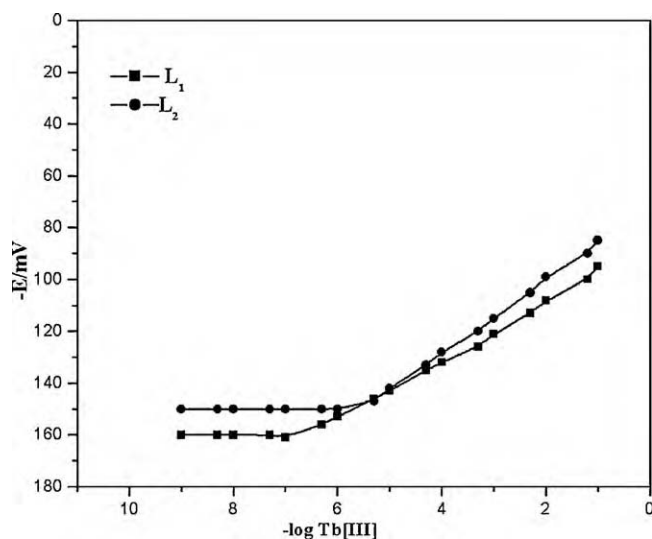
Fig. 5. Calibration plot of the terbium ion-selective sensor with ionophore L_1 and L_2.
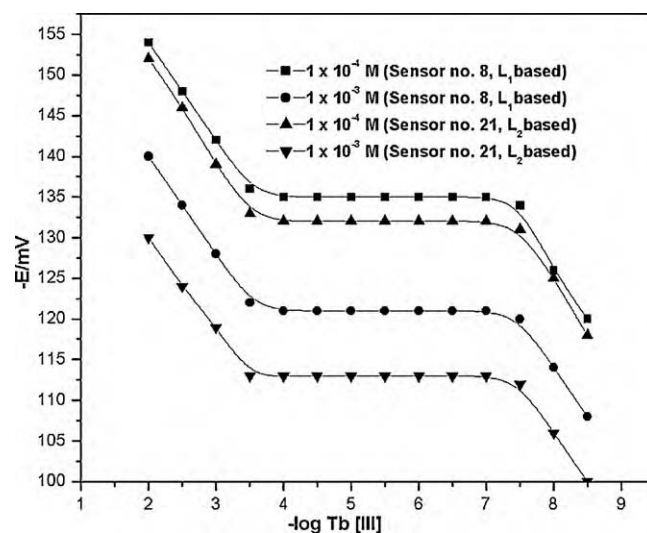
Fig. 6. Effect of pH on cell potential of sensor no. 8 (A) 1.0×10^{-3} M, (C) 1.0×10^{-4} M and sensor no. 21 at (B) 1.0×10^{-3} M, (D) 1.0×10^{-4} M Tb^{3+} solutions.
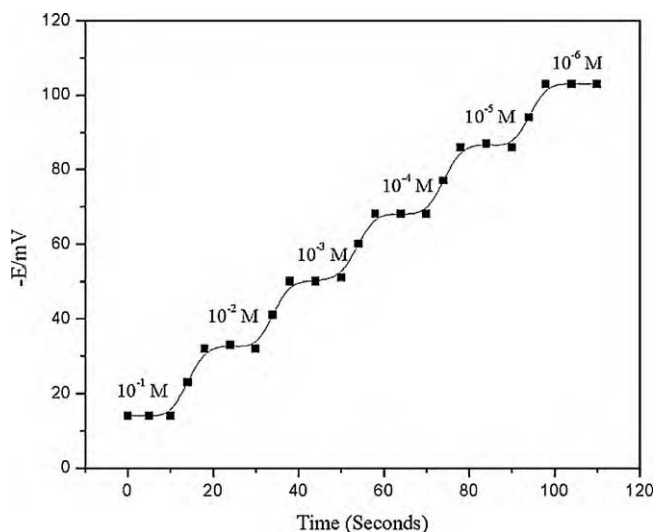
Fig. 7. Response time study of proposed sensor no. 8.

3.5. Determination of formation constant

A selective complexation of analyte ions by ionophores is primarily responsible for the selectivity of sensors. Despite the wide use of lipophilic and chemically immobilized ionophores in chemical sensor applications, only a limited number of experimental techniques are available to assess the binding strengths of these highly selective molecular probes directly in the polymeric matrix of the sensor. A different approach to measure complex stability constants in ISE membranes relies on recording electrical potential of segmented sandwich membranes [25]. Polymeric membrane sensors primarily respond to ion activities on both sides of the aqueous–organic phase boundary. The incorporation of an ion carrier into the membrane phase should induce a substantial potential change at the sample-membrane phase boundary, since the ion activity within the organic phase is dramatically altered. Therefore this effect could be used to determine the formation constant of the ion–ionophore complex.

It requires membrane potential measurements on two-layer sandwich membranes, where only one side contains the ionophore. If both membrane segments have the same ionic strength, it is convenient to assume that the activity coefficients for the complexed and uncomplexed ions are approximately equal. In that case, they can be omitted and the complex constant is related to the potential. In present studies the stability constants are investigated according to method proposed by Mi and Bakker [26] using the following equation:

$$\beta_{IL_n} = \left(L_T - \frac{nR_T}{z_I}\right)^{-n} \exp\left(\frac{E_M z_I F}{RT}\right)$$

where L_T is the total concentration of ionophore in the membrane segment, R_T is the concentration of lipophilic ionic site additives, n is the ion–ionophore complex stoichiometry and R, T and F are the gas constant, the absolute temperature and the Faraday constant respectively and an ion carries a charge of z_{I^-}. This relationship allows for the convenient determination of formation constants of ion-ionophore complexes within the membrane phase on the basis of transient membrane potential measurements on two-layer sandwich membranes. The knowledge of formation constants of the relevant complexes is beneficial to the process of optimizing the structure of ionophores and the composition of ISE membranes for given analyte ions.

The determined formation constants $\left(\log \beta_{IL_n}\right)$ for the examined different complexes are presented in Table 3. The elapsed time

Table 3
Formation constants of different Schiff base–metal complexes.

Metal ion	Formation constant $\left(\log \beta_{IL_n}\right)$	
	Schiffbase (L_1)	Schiff base (L_2)
Tb^{3+}	7.42	5.50
Lu^{3+}	2.23	2.12
Er^{3+}	3.63	3.55
Yb^{3+}	2.61	2.52
Sm^{3+}	3.54	3.40
Eu^{3+}	3.81	3.73
Ce^{3+}	1.96	1.73
Gd^{3+}	4.45	4.25
La^{3+}	1.25	1.13
Nd^{3+}	2.50	2.44
Ho^{3+}	3.98	3.80
Tm^{3+}	2.95	2.80
Cr^{3+}	1.05	0.98
Pb^{2+}	0.88	0.76

between sandwich fusion and exposure to electrolyte was typically <2 min. The potential was recorded as the mean of the last min of a 5 min measurement period in the appropriate salt solution. The potential of such sandwich membranes remains free of diffusion-induced potential drifts for about 20 min. Standard deviations were obtained based on the measurements of sets of at least three replicate membrane disks that were made from the same parent membrane. A careful analysis of the data in Table 3 reveals that terbium ion has significant cation-binding characteristics.

3.6. Potentiometric selectivity of the sensor

Selectivity is the most important characteristic that defines the nature of devices and the range to which it may be successfully employed. In this work the influence of interfering ions on the response behaviour of the terbium sensor was examined by fixed interference method (FIM) [27]. In this method, the electromotive force (emf) values were measured for solutions of constant activity of the interfering ion (1.0×10^{-4} M), a_B and varying activity of the primary ion, a_A in a cell comprising of an ion-selective electrode and a reference electrode. The emf values obtained were plotted versus the logarithm of the activity of the primary ion. The intersection of the extrapolated linear portions of the plot indicates the

Table 4
Selectivity coefficient values $\left(\log K^{Pot}_{Tb^{3+},B}\right)$ for terbium (III) selective sensors by fixed interference method (FIM).

Interfering ion (B)	Selectivity coefficients $\left[\log K^{Pot}_{Tb^{3+},B}\right]$ by FIM method	
	Sensor no. 8	Sensor no. 21
Lu^{3+}	-6.3×10^{-3}	-6.8×10^{-4}
Er^{3+}	-4.0×10^{-3}	-4.8×10^{-4}
Sm^{3+}	-4.2×10^{-3}	-4.7×10^{-4}
Yb^{3+}	-5.2×10^{-3}	-5.7×10^{-4}
Eu^{3+}	-3.8×10^{-3}	4.3×10^{-4}
Ce^{3+}	-6.6×10^{-3}	-7.1×10^{-4}
Gd^{3+}	-3.0×10^{-3}	-3.5×10^{-4}
La^{3+}	-6.0×10^{-4}	-6.6×10^{-4}
Nd^{3+}	-5.5×10^{-3}	-6.0×10^{-4}
Ho^{3+}	-3.6×10^{-3}	-4.1×10^{-4}
Tm^{3+}	-4.5×10^{-3}	-5.0×10^{-4}
Cr^{3+}	-3.0×10^{-5}	-4.2×10^{-5}
Al^{3+}	-3.4×10^{-5}	-4.5×10^{-5}
Pb^{2+}	-6.5×10^{-5}	-6.8×10^{-5}
Zn^{2+}	-7.2×10^{-5}	-7.5×10^{-5}
Na^+	8.5×10^{-5}	-6.0×10^{-4}
K^+	-9.0×10^{-5}	-5.0×10^{-4}

Table 5
Comparison of the results from the proposed sensor no. 8 and AAS.

Sample	Added (μg L^{-1})	Found by proposed sensor (μg L^{-1})	Found by AAS (μg L^{-1})	Recovery $\pm$ SD (%)*	t-Test ($P = 0.05$; $t_{theoritical} = 2.20$)
Roorkee city	50	50.05	50.80	100 $\pm$ 0.2	$t_{experimental} = 2.11$
	200	201.05	99.52	99.9 $\pm$ 0.1	$t_{experimental} = 2.09$
	500	502.0	500.32	500 $\pm$ 0.1	$t_{experimental} = 2.11$

*Triplicate measurement.

Table 6
The comparative study of proposed sensor (nos. 8 and 21) with the reported works.

S. no.	Working range (M)	Detection limit (M)	Slope (mV dec^{-1} of activity)	Ref.
1	1.0×10^{-5} to 1.0×10^{-1}	7.0×10^{-6}	19.8 mV	[8]
2	1.0×10^{-6} to 1.0×10^{-2}	7.4×10^{-7}	19.8 $\pm$ 0.3	[9]
3	1.0×10^{-6} to 1.0×10^{-1}	8.0×10^{-7}	19.7 $\pm$ 0.4	[10]
4	1.5×10^{-7} to 1.0×10^{-2}	9.3×10^{-8}	19.5	[28]
5	1.0×10^{-6} to 1.0×10^{-1}	8.6×10^{-7}	19.4 $\pm$ 0.5	[29]
6	3.5×10^{-7} to 1.0×10^{-2} (L_1), 3.1×10^{-6} to 1.0×10^{-2} (L_2)	1.2×10^{-7} (L_1), 2.3×10^{-6} (L_2)	20.0 $\pm$ 0.5 (L_1), 19.5 $\pm$ 0.5 (L_2)	Proposed work

value of a_A that is to be used to calculate $K_{Tb^{3+},B}^{Pot}$ from the following equation:

$$K_{A,B}^{Pot} = \frac{a_A}{(a_B)^{z_A/z_B}}$$

where both Z_A and Z_B have the positive charges of both ions.

The values of selectivity coefficients obtained for the proposed Tb (III) sensor are given in Table 4. It is seen from the table that the selectivity coefficient for interfering metals ions are sufficiently smaller than 1.0, indicating that the present sensor is significantly selective to Tb (III) over other ions.

3.7. Effect of non-aqueous content

The real samples may contain non-aqueous content, so the performance of the sensor was also investigated in partially non-aqueous media using 10, 15 and 20% (v/v) non-aqueous content in methanol-water, ethanol-water and acetonitrile–water mixtures. It was found that the membrane sensor did not show any appreciable change in working concentration range and slope in mixtures up to 15% (v/v) non-aqueous contents. However, above 15% non-aqueous content, potentials show drift with time. The drift in potentials in the organic phase may be probably due to leaching of the ionophore at higher organic content.

4. Analytical applications

4.1. Titration of copper solution with standard EDTA solution

This sensor was found useful as an indicator electrode in potentiometric titration of Tb (III) with EDTA. A 20 mL solution of 2.5×10^{-4} M Tb (III) was titrated against a 1.0×10^{-3} M EDTA solution. As indicated from Fig. 8, the sharp inflection point, showing perfect stoichiometry was observed in the titration plot. Thus, the sensor can be used to determine Tb^{3+} ion accurately under laboratory conditions.

4.2. Determination of terbium (III) in spiked water sample

The prepared sensor was effectively employed for the determination of Tb (III) in spiked water samples. Three water samples were prepared by addition of 100, 200 and 500 μg Tb (III) per liter in tap water of Roorkee city and analysis was done after adjusting pH to 5.0. The data presented in Table 5, shows that the results obtained by the proposed sensor are comparable with atomic absorption spectrometer and recovery is 99.9–100.
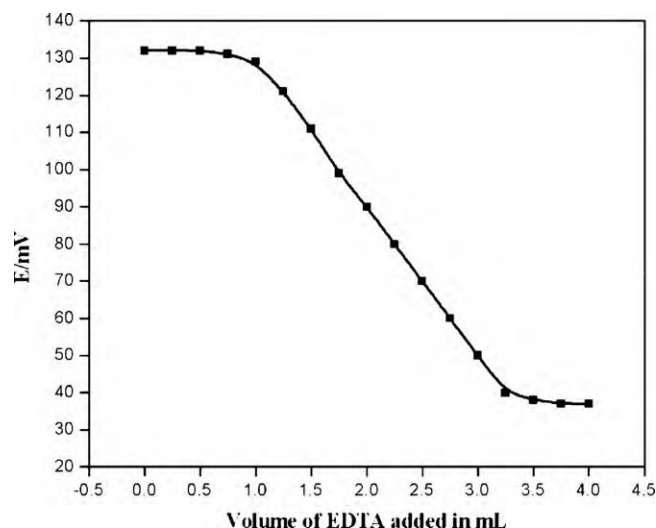
Fig. 8. Potentiometric titration curve for 20 mL of 1.0×10^{-4} mol L^{-1} terbium with 1.0×10^{-3} mol L^{-1} EDTA using the proposed sensor (no. 8).

5. Conclusion

The sensor based on L_1, ionophores exhibited wide working concentration range (3.5×10^{-7} to 1.0×10^{-2} M) low detection limit (1.2×10^{-7} M), high sensitivity, long-term stability (3 months) and fast response time (11 s) with Nernstian slope 20.0 $\pm$ 0.5 dec^{-1} activity. The selectivity of the membrane sensor toward Tb (III) ion is quite good for most of the cations and the response characteristics of the proposed sensors are better or comparable than those previously reported electrodes (Table 6) that makes it a superior potentiometric device. The sensor based on (L_1) offers a possibility for practical sensing in the determination of terbium (III) in variety of spiked water samples as well as in potentiometric titration of Tb (III) with EDTA.

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